Chapter 7

POLYURETHANE UREAS WITH HIGH TEAR STRENGTH AS BIODEGRADABLE POLYMERS

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Summary

Biodegradable polyester urethanes urea (PUU) were synthesized by terminating a 2000 g/mol molecular weight poly(?-caprolactone) prepolymer with three different diisocyante: L-lysine-ethylester-diisocyanate (LDI), 1,4-butanediisocyanate (BDI) and 1,6-hexanedi-isocyanate (HDI). The prepolymers were chain extended with 1,4-butanediamine. These polymers do not release toxic degradation products. Thermal and mechanical properties were determined. Due to phase separation and crystalline hard segments, BDI based PUU exhibit a very high tear strength of 161 kJ/m^2. Replacing BDI by HDI increases the tensile properties. It lowers the tear strength to 130 kJ/m^2 and increases the permanent set from 12% to 18.5% as a result of less ordered hard segments. Replacing the diisocyanate by LDI, causes phase mixing and soft segment crystallinity, which had a negative effect upon the mechanical properties. Porous materials with a compression modulus of 750 kPa were made of BDI based PUU. These materials seem to be suitable for meniscal prosthesis.

Introduction

Lesions of the knee joint meniscus are among the most frequent orthopaedic affections[1]. Removal of the meniscus, meniscectomy, was standard practice until it became clear that meniscectomy results in degeneration of articular cartilage. Nowadays partial meniscectomy is the method of choice but although the results improve, degeneration is not prevented[2].

Repair of meniscal lesions may be a better option since all meniscal tissue can be preserved. As a result of its limited vascularity, only lesions in the vascular periphery can be repaired adequately by simply suturing[3,4]. For lesions situated in the avascular part of the meniscus, no reliable methods for repair exist. Therefore, methods for cartilage repair are needed. A successful technique was found to be implanting of porous polyurethanes in the meniscus of dogs[5-8] . Using this method healing of meniscal lesions can be achieved in a substantial number of cases.

Polyurethanes were used for this application because of the excellent mechanical properties and reasonable blood compatibility and biocompatibility. First an polyurethane based on 4,4'-diphenyle-methane diisocyante (MDI) was used. Although the results turn out very satisfactory, this polyurethane will yield 4,4'-diaminodiphenylmethane (MDA) upon degradation which has been found to be mutagenic, carcinogenic, teratogenic and very toxic[9]. Although it has not been shown unambiguously that MDI-based polyurethanes induce the

formation of cancer and that MDA is formed upon degradation, it would be better to replace this component in the polyurethane formulation.

Therefore, in a previous study we used an aliphatic isocyante, 1,4-cyclohexane-diisocyanate (CHDI), and poly(?-caprolactone) based polyurethane[8]. Due to the symmetrical structure and the rigid rod-like shape of the isocyanate, the polyurethane was semicrystalline and possessed good mechanical properties. Porous materials of this polyurethane were also successfully used for meniscal reconstruction.

When the meniscus is too severely damaged to be treated by repair or partially meniscectomy, total meniscectomy is the only alternative. Because of the adverse effects of meniscectomy we, therefore, developed a porous polyurethane prosthesis suitable for replacement of a complete meniscus[8]. Due to the very high shear stresses to which a meniscal prosthesis is exposed, the stress hysteresis phenomenon that linear PU's are known to exhibit, could be of great consequence[10]. This phenomenon is attributed to a disruption of hard segments with strain, leading to permanent deformation. By chemical cross-linking the polymer this problem can be overcome.

Therefore an aliphatic PU network was synthesized by crosslinking a poly(?-caprolactone)/ CHDI based prepolymer with glycerol. Porous meniscal prostheses of this polymer were implanted into the knee joint of dogs but tearing out of the sutures has found to be a serious problem[11]. It appeared that the tear strength of the polyurethane network was much lower (20.8 kJ/m^2) than the tear strength of the linear aliphatic PU (114.0 kJ/m^2). A complex suturing technique was used to solve this tearing problem partially. After an induction time of 18 weeks the prostheses became filled with tissue strongly resembling normal meniscal tissue. Nevertheless increasing the tear resistance of the material seem to be a desirable route to improving the prosthesis.

The aim of this study is to synthesize polymers with high resistance to tear, which do not release toxic degradation products, suitable for meniscal reconstruction and meniscal prosthesis. In this study biodegradable polyester urethane ureas (PUU's) were synthesized. PUU's are known to exhibit good phase separation due to the polarity of the urea bond which improves the mechanical properties[12]. Three PUU were synthesized by a two step polymerization. In step one a 2000 g/mol molecular weight poly (?-caprolactone) prepolymer was terminated with three different diisocyante: 2,6-diisocyanto ethylhexanoate, reffered in this study as lysine diisocyanate (LDI), 1,6-hexanediiso cyanate (HDI) and 1,4-butane

diisocyanate (HDI). In step two the prepolymers were chain extended with 1,4-butanediamine which is present in cells of mammals[13]. It is a precursor, degradation and excretion product of polyamines which have many functions in various processes in living cells.

We determined the tear strength, tensile strength, stress hysteresis and thermal properties of these polyurethanes ureas and compared them to the properties of the aromatic and aliphatic PU that were used for meniscal reconstruction and prosthesis. BDI based PUU exhibited the highest tear strength and lowest stress hysteresis. Therefore, this polymer seem to be suitable for the application. Porous materials of this polymer were made using a freeze-drying/salt-leaching technique. Porous materials with a compression modulus up to 750 kPa could be made.

Experimental

Materials

Poly(?-caprolactone) diol (Mw=2000, Aldrich) was dried azeotropically with a tenth fold excess of toluene. The synthesis of ethyl 2,6-diisocyanatohexanoate (L-lysine-ethylester-diisocyanate LDI) has been described elsewhere[14]. 1,4-Butane diisocyante (BDI, Aldrich and DSM), 1,6-hexane diisocyante (HDI, Merrck-Schuchard), LDI, 1,4-butanediamine (BDA) and N,N'-dimethylformamide (DMF, Janssen Chimica) were distilled prior to use.

Polymer synthesis

Polymerizations were caried out without adding catalyst. The polymers were prepared in a two-step polymerization process under nitrogen atmosphere.

In step one poly(?-caprolactone) was dissolved in a six fold excess of BDI, HDI or LDI. The reaction mixture was stirred at 80^{o}C for two hours. Then the excess diisocyanate was removed under reduced pressure (0.01 mBar) in a Kügelrohr at 70^{o}C for two and four hours in the case of BDI and HDI, respectively. In case of LDI, the temperature was 90^{o}C and time three hours. Because not all the excess could be removed, the ratio NCO and OH groups was approximately 1.1.

In step two the prepolymer was dissolved in DMF at a concentration of 6 wt.-% and a dilute solution of BDA in DMF (1.4 wt.-%) was added slowly with good stirring at room temperature. The reaction mixture became viscous and stirring was continued at room temperature for another hour. In order to lower the viscosity of the solution, the temperature

was increased slowly to 160^{o}C. The polymer was precipitated in water. Then the polymer was dried at 40^{o}C under reduced pressure.

Polymer films

BDI and HDI based PUU were dissolved in DMF at 160^{o}C, LDI based PUU was dissolved in DMF at room temperature. Solution was poured into a petrish dish. The dish was heated to 50^{o}C until DMF was evaporated .

Polymer characterization

Intrinsic viscosity's were measured in m-cresol at 25^{o}C using an Ubbelohde viscosimeter. Thermal gravimetric analyses was performed on 1-5 mg film samples using Perkin Elmer TGA-7 equipment.

DSC thermograms over the temperature range of -100 ^{o}C to 250 ^{o}C were recorded with a scan speed of 10^{o}C/min using a Perking-Elmer DSC-7.

Dynamic mechanical analysis was performed using a Rheometrics RSA-II DMTA. In tension mode at a constant loading, films (0.35 x 3 x 35 mm^{3}) were subjected to an oscillating strain of maximal amplitude of 0.5% at a frequency of 1 Hz. Heating rate was 5 ^{o}C/min. Porous materials were subjected to an oscillation compression.

Tensile testing was performed on rectangular-shaped specimens (40 x 0.75 x 0.35 mm), cut from thin films at room temperature using an Instron (4301) tensile tester, equipped with a 100 N load-cell, at a cross-head speed of 10 mm/min. Tearing properties were determined using a Instron 4301 tensile tester. Trouser specimens of 3.75 long, 1.25 cm wide and a longitudinal slit of 2.5 cm were used. During testing the force was applied normally to the plane, operating a crosshead speed of 250 mm/min.

An ISI-DS-130 scanning electron microscope was used for studying the pore structure of the porous materials.

Preparation of porous materials

The polymer was dissolved in DMF at a concentration of 17% at 160 ^{o}C. Five mililiter of the solution was mixed with 0.77 g NaCl crystals (150 ?m - 300 ?m). The mixture was then rapidly cooled to room temperature where gel formation occurred. The gel was poured into 1,4-dioxane for six days to replace DMF. The degree of swelling/polymer concentration and

therefore the compression modulus could be controlled by adding non-solvent (c-hexane) to dioxane. After cooling to -15°C, solvent/non-solvent was removed under reduced pressure (0.05 mbar). NaCl crystals were removed by washing the polymer/crystal mixture with water.

Results and discussion

Polymers

The PUU's were synthesized by chain extending a diisocyanate terminated poly(?-caprolactone) (PCL) prepolymer with 1,4-butanediamine (BDA)[15]. For the synthesis of the prepolymer, PCL diol was dissolved in a six fold excess of BDI, HDI or LDI. The excess was used to limit the formation of PCL dimers, trimers etc. L-lysine-ethylester-diisocyante (LDI) was used because the degradation product of LDI, L-lysine, is non-toxic; in fact it is a essential aminoacid. 1,4-Butane diisocyante (BDI) was used because it will yield 1,4-butanediamine upon degradation, which is present in cells of mammals. In addition BDI is

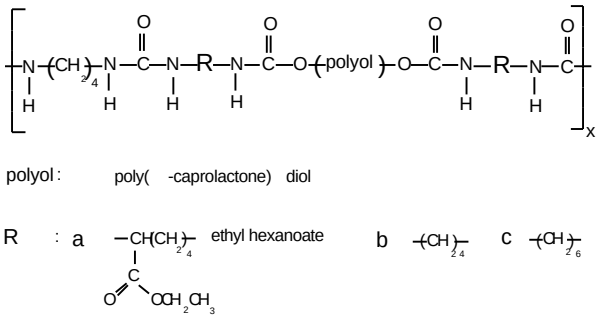

***Figure 1**. Chemical structure of polyurethane ureas; **a**, based on L-lysine diisocyanate; **b**, based on butanediisocyanate; **c**, based on hexanediisocyanate.*

expected to form good hard blocks with the chain extender. Hexamethylene diisocyanate (HDI) was used, although the toxicity of the HDI degradation product is not known, to observe the properties changes with small change of hard blocks, compared to BDI based PUU.

Table 1

	intrinsic viscosity (dl/g)	tearing energy (kJ/m^2)	permanent deformation (%)
Aromatic PU[1)]	-	47	10.5
Aliphatic PU, linear[2)]	-	114	11.5
Aliphatic PU, network[3)]	-	20.8	6.5
LDI based PUU	2.18	36	15.5
BDI based PUU	1.05	161	12.0
HDI based PUU	1.72	137	18.5

1) MDI/ adipic acid/ tetramethylene glycol based PU used for meniscal reconstruction
2) CHDI/ cyclohexane dimethanol/ poly(?-caprolactone) based PU used for meniscal reconstruction
3) CHDI/ glycerol/ poly(?-caprolactone) based PU network used for meniscal prosthesis

The chemical structures of the PUU's are presented in figure 1 and intrinsic viscosities are presented in table 1.

Thermal properties

Since the mechanical properties are largely influenced by the morphology, the thermal properties of the polymers were investigated. Thermogravimetric analysis (TGA) has been used to examine the thermal stability of the PUU's. The results are presented in figure 2. LDI based PUU is stabile to 250 ^oC, BDI and HDI based PUU stabile to 280^oC. Thus DSC and DMTA measurements can be recorded to 250 ^oC without degradation of the polymer.

DSC thermograms of PUU films are shown in figure 3. The DSC scan of the LDI based PUU exhibit a Tg at -52.1^oC and two melting endotherms at 40.5^oC and 90.9^oC with respectively, melting enthalpies of 15.9 J/g and 11.5 J/g. The Tg and lower melting temperature correspond to the soft segments. Since the fusion temperature of the poly(?-caprolactone) prepolymer is 60 ^oC, the higher melting temperature correspond, at least in part to the hard block sequences. The value of Tg is about 14 ^oC higher than the Tg of pure soft segment oligomer, indicating that there is some mixing of hard segments in the soft segment phase[16.17]. The DSC scan of BDI based PUU exhibits a Tg at -56.7^oC and two melting endo-

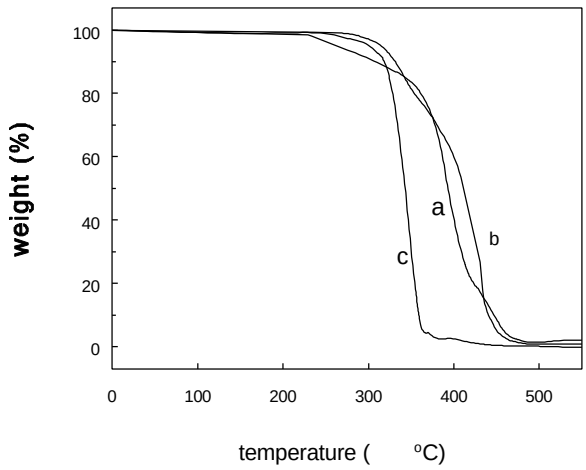

Figure 2*. TGA-curves of polyurethane ureas, (.....)a L-lysinediisocyanate based PUU, (___) b butanediisocyanate based PUU and (-----) c hexanediisocyanate based PUU.*

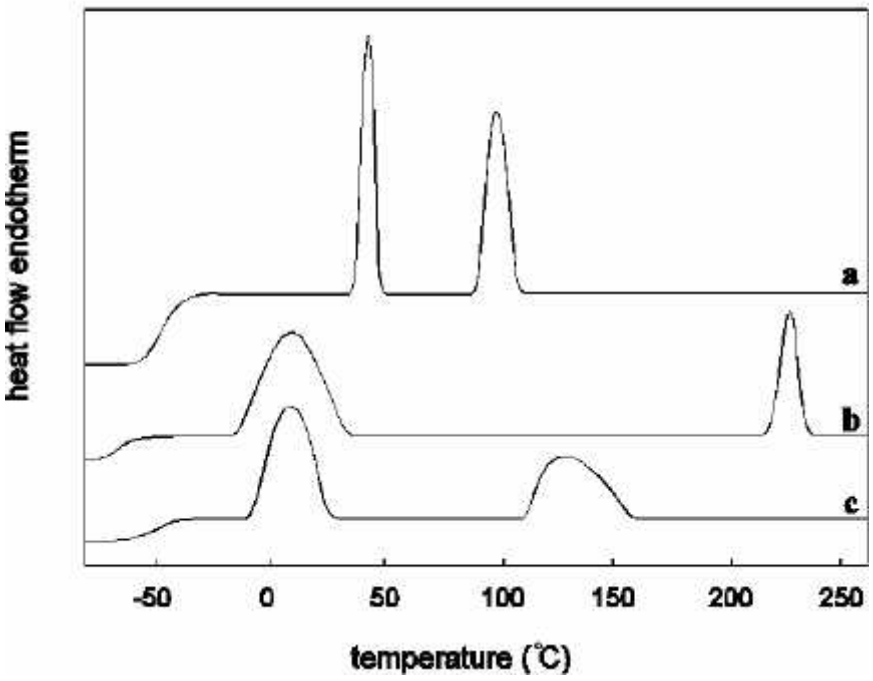

Figure 3*. DSC-curves of a: L-lysinediisocyanate based PUU, b: butanediisocyanate based PUU and c: hexanediisocyanate based PUU.*

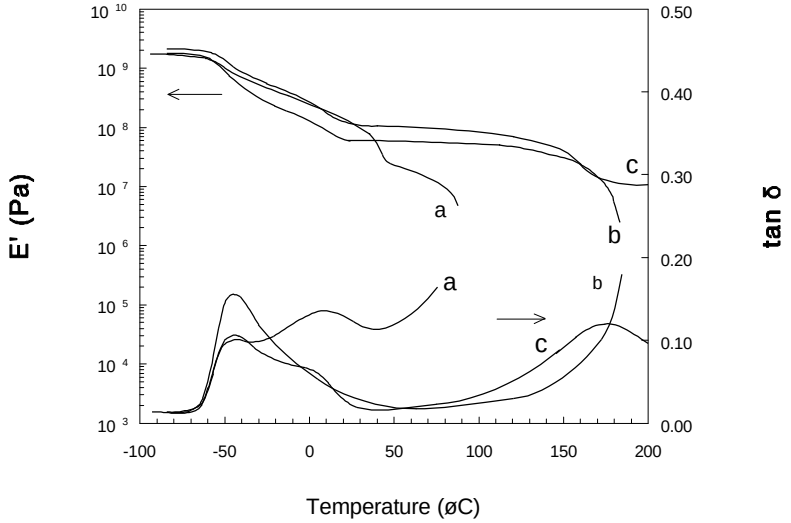

Figure 4*. Dynamical mechanical properties of (.....)(a) L-lysinediisocyanate based PUU, (___) (b) butanediisocyanate based PUU and (-----) (c)hexanediisocyanate based PUU.*

therms at 20.2°C and 218.5 °C with respectively melting enthalpies of 22.8 J/g and 10.5 J/g. The lower Tg is an indication for better phase separation. Apparently the hard segments are less compatible with the soft segment. The Tm for the hard segments is very high because BDI is expected to pack tighter with BDA. This results in a stronger interaction between the molecules in the hard domains.

The DSC scan of HDI based PUU exhibit a Tg at -51.0 °C, a melting endotherm at 21.5 °C with melting enthalpy of 17.3 J/g and a transition at 129 °C. Soft segments crystallinity can be compared to BDI based PUU. The higher Tg, compared to BDI based PUU, as well as the absence of a high melting temperature are indications for phase mixing. The transition at higher temperature correspond probably, according to Cooper et al., to the disruption of ordered segments[18]. Between the completely amorphous and perfectly crystalline states, there exist a continuum of ordered segment morphologies. This has been called a order-disorder transition[19].

The dynamic mechanical behaviour of the polymers is shown in figure 4. All the polymers exhibit a loss modulus transition at approximately -45°C corresponding to the soft segment glass transition. The LDI based PUU shows another loss peak at 20°C which is attributed to the melting of the crystalline phase of poly(?-caprolactone). For BDI and HDI based PUU's

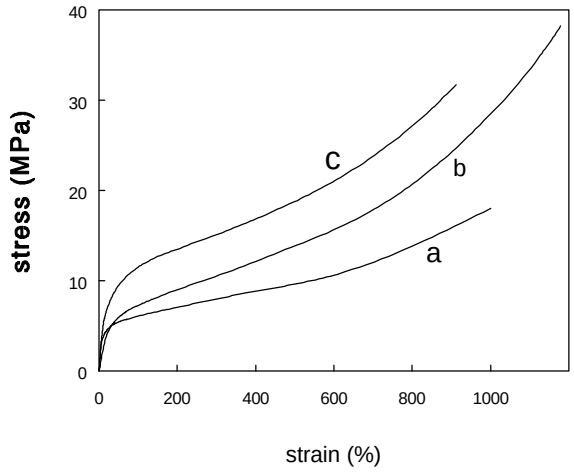

Figure 5*. Stress-strain behaviour of polyurethane ureas, (.....)(a) L-lysinediisocyanate based PUU, (____)(b) butanediisocyanate based PUU and (-----)(c) hexanediisocyanate based PUU.*

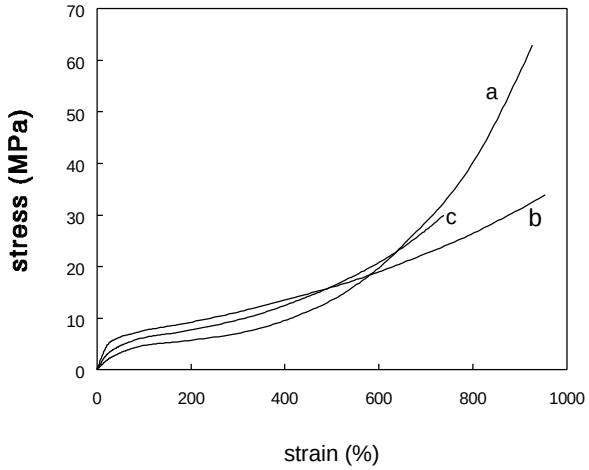

Figure 6*. Stress-strain behaviour of aromatic PU used for meniscal reconstruction (___)(a), linear aliphatic PU used for meniscal reconstruction (-----)(b) and linear aliphatic PU network used for meniscal prosthesis (.....)(c).*

this transition is observed as a shoulder at 5°C[16,20]. Poly(?-caprolactone) segments in BDI and HDI based PUU's are partially crystalline to 25°C, whether in the LDI based PUU they are crystalline to 50°C.

The LDI based PUU shows a small rubber plateau from 50°C to 80°C. At 90°C the hard segments of the LDI based PUU are melting, which corresponds with the DSC experiment. The BDI and HDI based PUU show a rubber plateau in the temperature range of 25°C to 150°C. For HDI based PUU this plateau is followed by a sharp drop in modulus at approximately 175°C. BDI shows a loss peak at 175°C. Thus, a small change of diisocyante structure has a considerable effect upon the thermal properties of the polymer. Noteworthy is the fact that during the synthesis of the polymers, removal of the excess HDI was more difficult than removal BDI. This might have caused some branching, which is likely to contribute to the different thermal behavior of the polymers.

Tensile properties

Tensile properties of the PUU are presented in figure 5. Tensile properties of polyurethanes which have already been used for meniscal reconstruction and meniscal prosthesis are presented in figure 6. The LDI, BDI and HDI based PUU's have a respective Young's modulus of 40, 52 and 38 MPa tensile strength of 17, 29 and 38 MPa, and a respective strain at break of 800, 1042 and 1168%. The stress-strain behaviour of BDI based PUU is comparable to the linear aliphatic polyurethane used for meniscal reconstruction. The higher strain at break of HDI based PUU compared to BDI based PUU is due to less ordered hard domains because deformation of the hard segment is easier[21]. This is also the reason for the higher tensile strength. Orientation of the polymer chains takes places under stress.

The high Young's modulus of BDI based PUU is a result of crystalline hard domain. There is only a very small contribution of crystalline soft segments to modulus at 20°C for BDI and HDI based PUU's. The crystalline soft segments partially determine the Young's modulus of LDI based PUU. DMTA shows a large contribution to modulus of soft segments at 20°C. The low tensile strength of this PUU is due to the lack of well ordered hard segments.

The curves of HDI and BDI based PUU's show a upturn at high strain which is indicative of strain induced crystallization[22]. To determine whether the soft segements of the polymers crystallize under strain, films were strained to failure which resulted in a certain permanent deformation. Figure 7 shows the thermograms for strained polymers. The melting temperature of the soft segments in BDI and HDI based PUU increased to 46°C, which is an indication

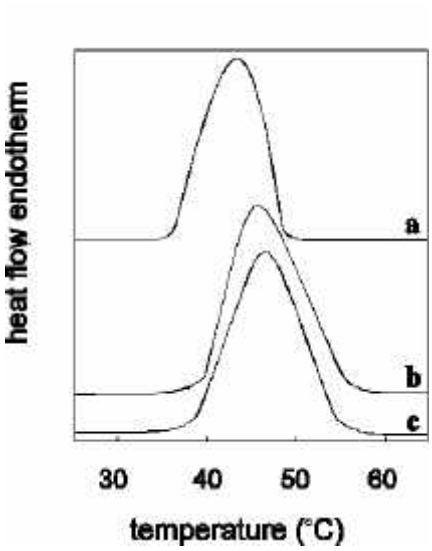

Figure 7*. DSC-curves of strained polyurethane urea films,* ***a****: L-lysinediiso-cyanate based PUU,* ***b****: butanediisocyanate based PUU and* ***c****: hexane-diisocyanate based PUU.*

crystallization under strain. The samples were scaned up to 250°C and no additional melting peak could be discerned. Hard segment disruption takes places under strain. The strain has hardly any effect upon the soft segment Tm of LDI based PUU; it increased to 43°C before. Apparently the tensile properties of LDI based PUU are limited by the lack of well ordered hard segments and soft segment crystallinity.

Permanent set

The permanent deformation is an important parameter since it is directly related to the hysteresis phenomenon[23]. Permanent deformation may shorten the time to material failure. In figure 8 the hysterese experiment is shown. The film is deformed cyclically up to 50% initial strain. Cycle A is the first cycly, B the 20th. After a recovery time of 2 hours, cycle C was recorded. At the beginning of cycle C the permanent set is determined. The permanent sets of the PUU and PU are presented in table 1. Permanent set of BDI based PUU is 12% and can be compared to the linear aliphatic PU used for menisical reconstruction. Permanent set of HDI based PU is 18.5% due to lack of crystalline hard blocks. The permanent set of LDI based PUU is 15.5% and is an intermediate between BDI and HDI PUU's, probably due to the soft segment crystallinity. As expected the polyurethane network shows the smallest permanent set since the hard segments are not able to deform through crosslinking.

Tear resistance

In a previous study we concluded that the resistance to tear is very important to prevent the sutures from tearing out of the material. Polymer networks show small resistance to tear because in such one-phase elastomers microcrack, once formed, encounter little resistance to growth because the network chains are highly mobile[24]. Eventually strain-induced crystallization can occur which increases the resistance to tear[25]. Blockcopolymers, however, show a higher resistance to tear because additionally to strain-induced crystallization, two processes can occur to impede crack growth. First the domains containing hard segments can be deformed and secondly their morphology can change which results in orientation.

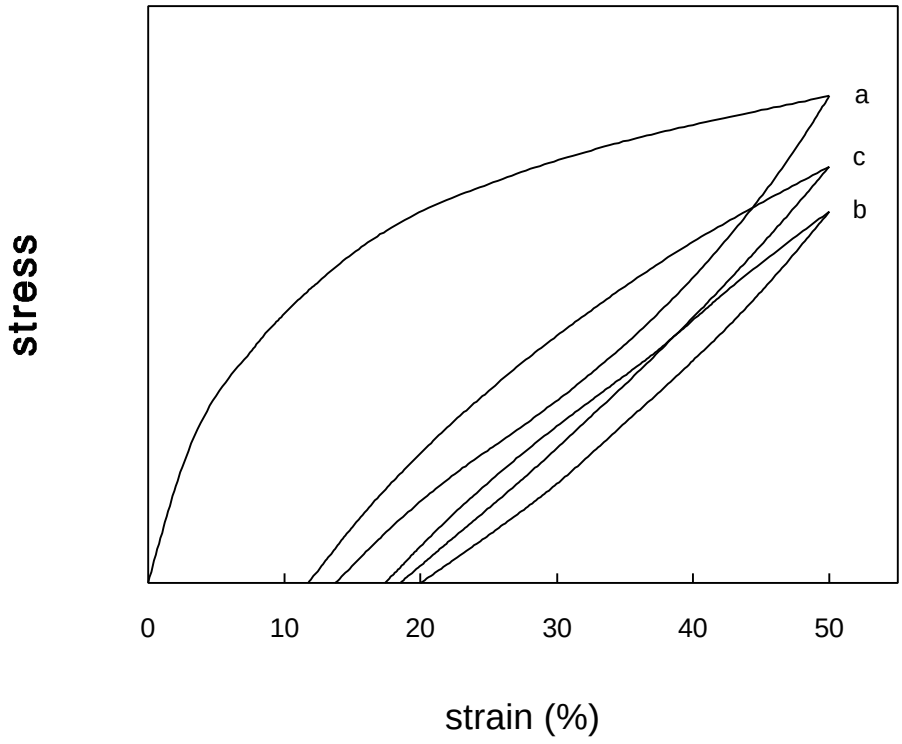

Figure 8*. Three consecutive deformation cycles up to 50% strain.* ***a****, first cycle;* ***b****, 20th cycle;* ***c****, 21th cycle. Recovery time between cycle b and c is two hours.*

There are several factors that determine the resistance to tear. In the case of polymer networks, tear strength G_c increases with increasing molecular weight between crosslinks M_c[26,27]. However no quantitative fit of G_c ? $M^{1/2}$, derived from the theory of rubber elasticity, is possible. This can be accounted for the fact that tear energy arising from viscoelastic effects depends upon the degree of crosslinking. Additionally, the effect of strain-induced crystallization is more pronounced at high M_c. According to Flory[28], the Tm on stretching is inversely related to heat of fusion (? H). Thus, the smaller value of ? H the greater will be the tendency to exhibit strain-induced crystallization.

For blockcopolymers the dependence of tear strength upon M_c is probably different. Two opposite effect may be observed. Higher M_c give rise to strain-induced crystallization but at the same time the concentration hard segments decreases which will lower the resistance to tear. The net effect is likely to depend upon the structure of hard and soft segments.

***Figure 9**. SEM micrograph of porous polyurethane urea based upon butanediisocyanate with a porosity of 84% (**a**) and 79% (**b**).*

The tear energy can be described by[29]:

$$G = 2F/h$$

where F is the applied force and h is the width of the torn path.

Tear energies of PUU's and PU's are presented in table 1. The LDI, BDI and HDI based PUU exhibit a tear strength of 36 kJ/m^2, 161.4 kJ/m^2, and 137 kJ/m^2, respectively. BDI based PUU shows a very high resistance to tear as a result of phase separation. The tear strength of HDI based PUU is somewhat lower but still higher than for linear aliphatic PU. The low tear energy of LDI based PUU is due to poor packing of the hard segments. LDI is a bulky molecule with an ester bond and is likely to be more compatible with ?-caprolactone segments than HDI and BDI. Additionally, this polymer lacks the ability to crystallize under strain because soft segments are already crystalline at ambient temperature.

Taking into account all the properties of the PUU's, the BDI based PUU seem to be the most appropriate polymer for meniscal prosthesis. Although the tensile strength is not as high as for HDI based PUU, it has a relatively low permanent set and a ultimate high tear strength. Additionally the polymer will release only non-toxic degradation products.

Crystalline remnant of the PUU in the last stage of degradation may be of concern but the crystallites in the BDI based PUU are rather small. The length of the hard segments, containing two BDI molecules and one BDA molecule is maximal 20 Å[22]. The thickness of the crystallites will be even less. Due to the high surface-free energy, these crystallites are more susceptible to degradation.

Porous material

In previous studies, porous polyurethanes were successfully used for meniscal reconstruction and meniscal prosthesis[5-8]. For the ingrowth of meniscus-like tissue, macropores of 150-300?m were found to be important. A combination of freeze-drying and salt-casting has proven to be an excellent method for preparing reproducible porous polymers[30]. The porous structures contained macropores, owing to the casting material, dispersed in a matrix of micropores which arised from freeze-drying the solvent. The porosity could be varied by changing the polymer and crystal concentration. Freeze-drying is possible when the polymer is soluble in a solvent that can be sublimized under reduced pressure, such as 1,4-dioxane, benzene or c-hexane. However, BDI based PUU is not soluble in a suitable solvents. Therefore, the polymer was first dissolved in DMF to a concentration of 17% at 160^{o}C. The high temperature was necessary to obtain a high polymer concentration and to decrease the viscosity of the solution. The polymer solution was mixed with NaCl crystals of 150?m - 300?m. After reducing the temperature, a gel was formed. The gel was poured into 1,4-dioxane in order to replace DMF. No shrinkage of the gel could be observed. After freezing-drying and washing out the NaCl crystals, the porosity of the material was 84%. Figure 9a shows a scanning electron micrograph of the porous structure. The compression behavior of this material and meniscal tissue of dogs is shown in figure 10. The material had a compression modulus of 150 kPa and is alike the modulus of the meniscal prosthesis, implanted in a previous study[8].

Due to the low compression modulus of the prostheses, compared to the modulus of meniscal tissue of dogs, degenerative changes of the articular cartilage were observed[31]. Although it was less severe than after total removement of the meniscus, a higher modulus is needed to protect the articular cartilage. Additionally, in case of meniscal reconstruction with porous copoly(L-lactide/?-caproalctone), we observed that the ingrowth of cartilage, was affected by the compression modulus/density of the material. In materials with higher modulus, a higher percentage cartilage was formed.

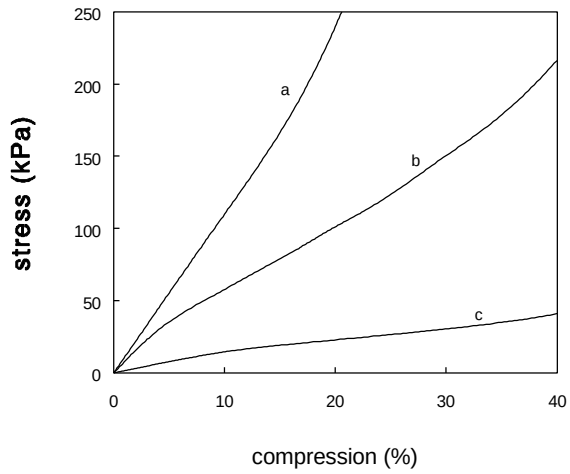

***Figure 10**. Compression behavior of mensical tissue of dogs (_____)(a), porous butanediisocyante based PUU with porosity of 84% (.....)(b) and porous BDI based PUU with porosity of 79% (------)(c).*

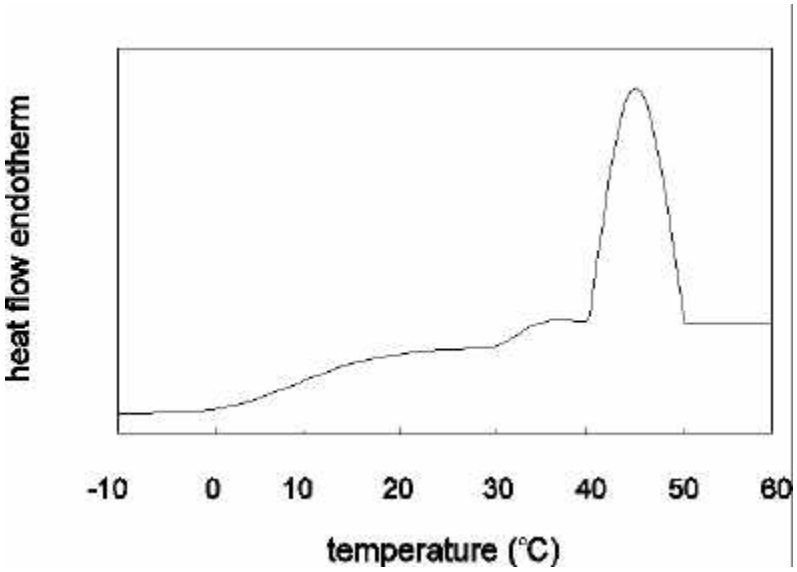

***Figure 11**. DSC-curve of porous material made of butanediisocyanate based PUU.*

In order to increase the polymer concentration in the gel, 25% non-solvent (c-hexane) was added to 1,4-dioxane. This resulted in shrinkage of the gel mixture, a lower porosity of the porous material (79%) and an increase of the Young's modulus to 750 kPa shown in figure 10. The compression modulus at 20% compression was 500 kPa. In figure 9b the porous structure of the material is shown.

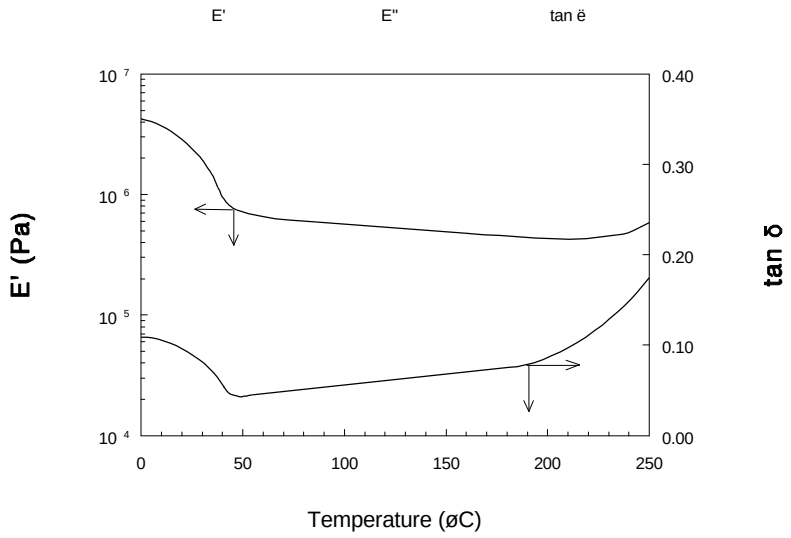

***Figure 12**. Dynamical mechanical properties of porous butanediisocyanate based PUU.*

The morphology of polyurethanes is, however, very sensitive towards thermal history[18]. Since the thermal history of the porous material differs from the thermal history of the polymer films, it is likely that the morphology of the porous material and film is different. The DSC thermogram of porous BDI based PUU is shown in figure 11. The Tg and and soft segment Tm increased to respectively 7.2 ^{o}C and 48.4 ^{o}C. Furthermore, no Tm of the hard segments could be observed. These are indications that the hard and soft segments are phase mixed to a high degree.

Figure 12 shows a compression DMTA scan of a porous material. Although it is difficult to evaluate the values of compression moduli from the plot qualitatively, it can be observed that the temperature has a large effect on the compression modulus in the range of 20^{o}C to 45^{o}C. Therefore the phase mixing, as a result of the production process of porous materials, should be prevented. In order to do so, after removing DMF from the gel, the polymer/dioxane/c-hexane/crystall mixture was heated to 70^{o}C allow phase separation. Afterwards the temperature was decreases very slowly and the solvent/non-solvent mixture was removed by freeze-drying. Afterwards, the thermal properties of the porous polymer were comparable to properties of the polymer film while the porosity and porous structure have not been changed. Therefore, this material seem to be suitable for meniscal reconstruction and meniscal prosthesis.

Conclusions

A polyurethane urea based upon poly(?-caprolactone), 1,4-butanediamine and butanediisocyanate (BDI) has been found to be semicrystalline polymer with good mechanical properties. The tensile properties and permanent set were comparable to properties of a linear polyurethane based upon poly(?-caprolactone) and cyclohexanediisocyanate (CHDI) used for meniscal reconstruction. It exhibit a relatively high tear strength due to hard segment crystallinity. Replacing BDI by hexamethylendiisocyanate (HDI) resulted in a higher strain at break and higher tensile due to less ordered hard segments. It, however, increased the permanent set remarkably. Thus a small change of diisocyante structure has a considerable effect upon the morphology of the polymer. Replacing the diisocyanate by L-lysine diisocyante causes phase mixing. Due to the soft segment crystallinity and the lack of well ordered hard segments the polymer showed poor mechanical properties. For a combination of low permanent set and high tear strength, which is essential for meniscal prosthesis, tightly packed crystalline hard segments are necessary. BDI based PUU seem to be suitable for that application. The crystallites of hard segments are very small and not likely cause problems during degradation.

Porous of this material can be made by the combination of freeze-drying and salt casting. By varying the solvent/non-solvent content, the swell grade and thus the porosity and stiffness of the porous materials can be controlled. Since with this method high compression modulus materials can be made and the polymer will only releases non-toxic products upon degradation, these materials seem to be appropriate for meniscal prosthesis.

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